Assistance Agreement Quarterly Report Summary: 15th Quarter

Title: **Baltimore Supersite: Highly Time and Size Resolved Concentrations of Urban PM2.5 and its Constituents for Resolution of Sources and Immune Responses**

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Research Category: Particulate Matter Supersites Program

Project Period: January 15, 2000 to December 31, 2004

Objectives of Research: Our primary objectives are to i) provide an extended, ultra high-quality multivariate data set, with unprecedented temporal resolution, designed to take maximum advantage of advanced new factor analysis and state-of-the-art multivariate statistical techniques; ii) provide important information on the potential for health effects of particles from specific sources and generic types of sources, iii) provide large quantities of well characterized urban PM for retrospective chemical, physical, biologic analyses and toxicological testing, iv) provide sorely needed data on the sources and nature of organic aerosol presently unavailable for the region, v) provide support to existing exposure and epidemiologic studies to achieve enhanced evaluation of health outcome-pollutant and -source relationships, and vi) test the specific hypothesis listed in our proposal.

ACTIVITIES AND FUTURE PLANS
During the 14th report period the following activities were performed.
    1. **Spectrometer data.** Forward-Scattering Laser Spectrometer data collected at FMC and Clifton Park have been normalized and made ready for loading into the BSSDB.
    2). **SEAS samples.** 7 days of SEAS samples (about 330 samples) collected during the November 2002 (November 19-22 and 24-26), intensive have been analyzed for 11 elements

by Graphite Furnace Atomic Absorption Spectrometry. Analyses of a total of approximately 1200 30-min SEAS slurry samples collected at the three Baltimore supersite locations (FMC, Clifton Park, Ponca St.) have been completed. Three days worth of samples collected during the February 2003, mini-intensive (Feb 19-23) have been selected for analysis.

3. **Ponca St. Harvard Monitor Sulfate Data.** The Harvard-type semi-continuous sulfate analyzer usedat PONCA st. required calibration against filter data results obtained from Ion Chromatography analyses. Previously, analyses had been completed only for 24-hr speciation samples collected during the July and November 2002 intensives. To provide for additional calibration periods, several additional 24-hr filter samples were analyzed for sulfate by Research Triangle Institute using Ion Chromatography. Calibration factors have now been developed for these data and have been used to correct the remaining sulfate data in the BSSDB using a database application. With this, we have now completed all corrections to the Ponca St. Sulfate data. Final corrected concentrations have been loaded into the Baltimore Supersite Database. "Reasonableness"checks on the data will be completed in the next quarter. Detailed descriptions of the data analysis and correction protocols are given below.

3. **NARSTO submissions.** Previously, all data collected in 2001 (Clifton and FMC sites) have been submitted to the NARSTO archive. All LIDAR data have been submitted to the NARSTO archive. All remaining 2002 is being submitted by Clarkson. Clarkson University is reviewing the data files that they have submitted to NARSTO. There are clearly some problems with some of the files and these will need to be corrected. They need to compile files for the 2002 data and begin to get them submitted to the archive. They will be making an effort to catch up with the data submission requirements during this coming quarter.

4. **Publications.** We have submitted the following publications during the third and fourth quarters of 2003:

> Highly-time resolved particulate nitrate measurements at the Baltimore Supersite, by Harrison, D., Park, S. S., Ondov, J. M., Buckley, T., Kim, S. R., Jayanty, R. K. M., submitted to Atmospheric Environment.
>
> Atmospheric boundary layer structure as observed during a haze event due to forest fire smoke, by M. Pahlow, J. Kleissl, M. B. Parlange, J. M. Ondov and D. Harrison Submitted to Boundary Layer Meteorology.
>
> Tolocka, M. P., Lake, D. A., Johnston, M. V., Wexler, A. S. Number concentrations of fine and ultrafine particles containing metals, submitted to Atmos. Environ.

Drafts of manuscripts, submitted or in preparation may be downloaded from:
ftp\\Fatboy\D\InetPub\FTPRoot\Incoming

We continue to prepare manuscripts for publication based on individual investigator results and plan to begin integrated, multi-investigator data analyses in the next quarter.

We expect to submit the following new manuscripts for publication in the next quarter:

UMCP: A manuscript on 30-min data from the UMCP SEAS is in preparation.

Park, S. S., Pancras P. J., Ondov, J. M., Poor, N. A New Pseudo-deterministic Multivariate Receptor Model for Accurate Individual Source Apportionment Using Highly Time-resolved Ambient Concentrations Measurements, prepared for submission to JGR.

Park, S. S., Ondov, J. M., Carbon species and CO emission factors derived from the Canadian forest fires. To be submitted to the special JGR issue in January 2004.

Park, S. S., Harrison, D., Ondov, J. M., Seasonal and short-term variations in Nitrate concentrations. Seasonal and short-term variations in Nitrate concentrations.

Clarkson: Application of Expanded Factor Analysis Models to Identify the Source Washington DC Aerosol, B. Begum, W. Zhao, and P.K. Hopke

Baltimore Supersite: Highly Time and Size Resolved Concentrations of Urban Pm2.5 and its Constituents for Resolution of Sources and Immune Responses J.M. Ondov, T.J. Buckley, P.K. Hopke, M.B. Parlange, W. F. Rogge, K. S. Squibb, M.V. Johnston, and A. S. Wexler,

UDE/UD: M. P. Tolocka et. al., Particle classes in Baltimore, to be submitted by the end of January to the special JGR issue.

Murray Johnston Group: Size resolved ultrafine particle composition analysis part 3: Baltimore. To be submitted to the special JGR issue in January 2004.

UMAB: Mitkus R. J, Powell J. L, Ondov, J. M., Pancras, J. P. and Squibb KS. Baltimore $PM_{2.5}$ daily and seasonal variations in *in vitro* stimulated chemokine and cytokine release: Correlation with metal content. In preparation

JHU: Mariana Adam, Markus Pahlow, Vladimir A. Kovalev, John M. Ondov, Marc B. Parlange, Aerosol optical characterization by nephelometer and lidar during the Baltimore PM Supersite, 4 - 12 July 2002*, in revision following review for publication in* JGR Atmospheres.

5. **Detailed meteorological summaries** for major events identified during 2002 were prepared in the previous quarters. The list and website url for assessing detailed descriptions is provided below for the benefit of the Supersites participants.

6. **Data loading.** LIDAR derived- particle concentration data (relative concentration, time step, and range) have bee loaded in to BSSDB. Synchrotron XRF analyses results received for August 7-14 2001 will be loaded into BSSDB in January of 2004. Concentrations of 27 elements were reported at 30 minute intervals for 8 size ranges.

7. **SIRDB.** We have received all AQS data, Profiler data, and Supersites data from the NARSTO archive. Many formatting and data errors in some of the Supersites NARSTO data files were discovered. NARSTO was notified of these and new files are being created. Many database table definitions were redesigned to increase performance. The primary query function which provides the most flexible and detailed criteria specification and query generation was completed and is in beta test. Approximately 10 GB of data have been loaded.

METEOROLOGICAL SUMMARIES:

Meteorological summaries were prepared during the previous quarter and can be located at

http://www.jhu.edu/dogee/mbp/supersite2001/metsummary/summary.htm

Periods encompassing elevated PM events observed during the BSS study in 2002 are listed in Table 1. A chronological description of one of the episodes is presented below as an example.

Table 1 List of high PM events during 2002

Days (EST in 2002)	Features	24-hr PM2.5 ug/m3	Lidar	3D-sonic anemometer
4/17 – 4/18	Nitrate transient, high EC, OC	no TEOM	no	yes
6/10 – 6/11	High nitrate peak (~11 mg/m3) in the morning of June 11 due to high RH High sulfate peaks (13~15 mg/m3)in the afternoon of both June 10 & 11 due to high ozone	no TEOM	no	no
6/24 0900h – 6/26 0600h	High sulfate peak (~ 28 ug/m3) over the period with high Ozone	on TEOM	no	no
7/2 0900h – 7/3 0700h	High sulfate peak (~25 ug/m3) over the period with high Ozone	no TEOM	7/3	no
7/6 1900h – 7/9 1900h	Canadian Smoke: very high OC, high sulfate peak (~18 ug/m3) for 7/9 1000h–1500h due to high ozone	7/6 29.1 7/7 85.6 7/8 55.6 7/9 44.0 event: 64.8	7/6, 7/7, 7/8, 7/9	no
7/15	Nitrate transient		yes	no
7/18 0230h – 7/19 2200h	High sulfate peak (~24 ug/m3)	7/18 51.5 7/19 47.1	7/18	no

|		event: 51.5		
8/12 0900h – 8/14 1500h	High sulfate (24 ug/m3) & OC and high Ozone (possibly secondary OC produced in the afternoon)	8/12 39.5 8/13 57.1 8/14 37.8 event: 51.9	8/12, 8/13, 8/14	yes
10/3 1700h – 10/4 1400h	ECOC, nitrate, sulfate peak at nighttime of October 3 observed	10/3 37.3 10/4 39.5 event: 43.9	no	yes
11/20 – 11/21	Nitrate, ECOC transient		no	yes
11/29	OC transient		no	yes

LIDAR DATA

Johns-Hopkins has transferred all of the LIDAR data to the Narsto archive. A webpage structure (http://www.jhu.edu/~dogee/mbp/supersite2001/lidar_data.htm) was constructed during the privious quarter and was sent to NARSTO for validation. Mixing height calculations for the lidar data have been completed. For some days the data quality was not sufficiently good to allow determination of the mixing height. The time series of mixing layer height are accessible at

http://www.jhu.edu/dogee/mbp/supersite2001/lidar_data.htm

An html based data archive has been created for the NARSTO database. On a total of 4 CDs all raw lidar backscatter data, images, and mixing layer heights can be accessed. These CDs are available from the NARSTO database administrators. Please contact hookla@ornl.gov.

Aerosol Extinction. Highly resolved spatial and temporal lidar backscatter data obtained during the Baltimore Supersite
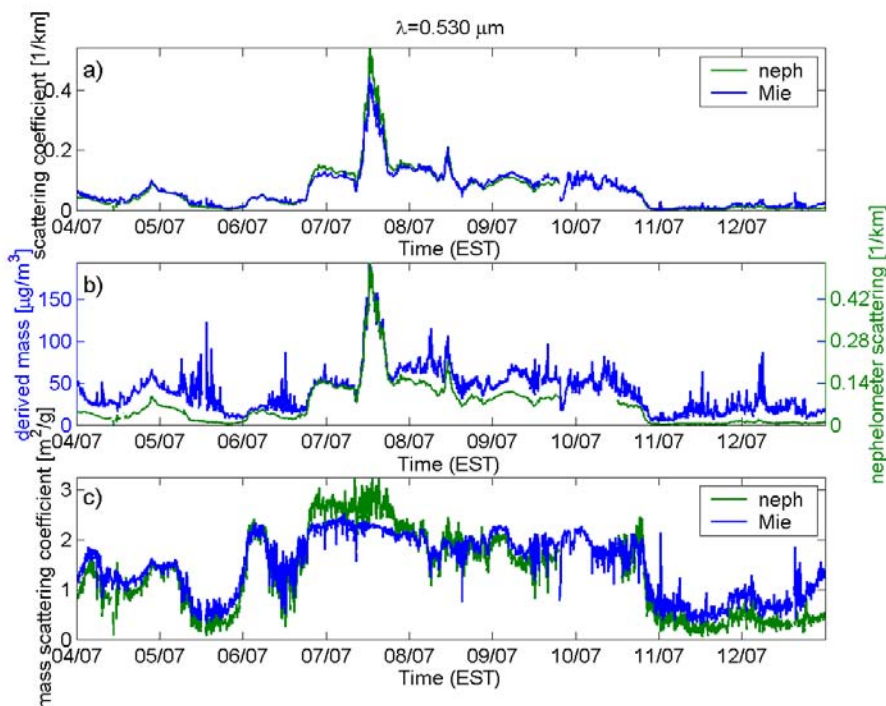
Figure 1. **Temporal variation of the aerosol scattering coefficient as measured by nephelometer and computed by Mie theory (a), of the derived mass (b) and of the mass scattering coefficient (c). Tick marks on the time axis correspond to midnight.**

study were analyzed with a near end approach to determine vertical profiles of the aerosol extinction coefficient during a period (4-12 July 2002) encompassing smoke fumigation from the Canadian forest fires (Figure 1).

The approach takes into account the aerosol scattering measured at ground level, obtained with a nephelometer at 0.530 µm, the ground level particle size distribution measurements (with SMPS and APS) and the calculated refractive index to determine the boundary condition using Mie theory. In addition to the vertical profile of the aerosol extinction coefficient, we compare the aerosol scattering coefficient at ground level, measured by the nephelometer, with related parameters, specifically derived mass concentration and the mass scattering coefficient. The index of refraction is chosen such that the measured and computed scattering coefficients match (such that the correlation coefficient between measured and computed aerosol scattering at 0.530 µm is $R = 0.98$). The chosen index of refraction for aerosol is 1.5-0.47i, which is typical for soot. The measured aerosol scattering coefficient by nephelometer at 0.530 µm ranged from σ_p=0.002 km^{-1} to σ_p=0.541 km^{-1}, whereas the aerosol

extinction coefficient computed with Mie theory (based on size distributions and refractive index) at 0.530 µm ranges from κ_p=0.010 km^{-1} to from κ_p=1.050 km^{-1}. The derived mass concentration is defined as the average density (here 1 gm^{-3} corresponding to soot) multiplied with volume size distribution (derived from particle number distribution measured with SMPS and APS). It was between 3.96 µg m^{-3} and 194.00 µg m^{-3}. The mass scattering coefficient is defined as the ratio between scattering coefficient and mass derived and it was between 0.058 m^{2}g^{-1} and 3.260 m^{2}g^{-1}. A discrepancy between mass scattering calculated using measured and computed scattering exists as the measured and computed scattering do not match perfectly. The mean and standard deviation of the two can be seen in Table 2.

Table 2. Mean and standard deviation for measured (nephelometer) and computed (Mie theory) aerosol scattering, computed (Mie theory) aerosol extinction coefficient, derived mass and mass scattering coefficient (using measured and computed scattering coefficient)

		4 July 00:00 EST – 6 July 18:00 EST	6 July 18:05 EST – 10 July 21:00 EST	10 July 21:05 EST – 12 July 23:55 EST
Measured aerosol scattering F_p [km^{-1}] (nephelometer)	Mean	0.032	0.126	0.006
	Standard deviation	0.019	0.080	0.003
Computed aerosol scattering F_p [km^{-1}] (Mie theory)	Mean	0.039	0.126	0.013
	Standard deviation	0.020	0.066	0.007
Computed aerosol extinction κ_p [km^{-1}] (Mie theory)	Mean	0.107	0.306	0.047
	Standard deviation	0.049	0.146	0.027
Derived mass M [µg m^{-3}]	Mean	30.1	59.6	17.3
	Standard deviation	14.5	27.0	9.83
Mass scattering F_p/M [m^{2}g^{-1}] – nephelometer	Mean	1.1	2.05	0.365
	Standard deviation	0.533	0.495	0.147
Mass scattering F_p/M [m^{2}g^{-1}] – Mie theory	Mean	1.34	2.08	0.762
	Standard deviation	0.470	0.270	0.248

The period analyzed was divided into three sub intervals corresponding to the periods before, during and after the haze event. Table 2 shows the mean and standard deviation for measured (nephelometer) and computed (Mie theory) aerosol scattering, computed (Mie theory) aerosol extinction coefficient, derived mass and mass scattering coefficient (using measured and computed scattering coefficient) for the 3 periods. The main remark is the increasing of the optical parameters during the second period (period of the haze event due to the Canadian forest fires).

The optical parameters as recorded or computed at ground level were compared with other studies done in similar conditions (e.g. Carrico, C. M., M. H. Bergin, J. Xu, K. Baumann, H. Maring, Urban aerosol radiative properties: Measurements during the 1999 Atlanta Supersite Experiment, J. Geophys. Res., 108(D7)8422, doi:10.1029/2001JD001222, 2003 ; Hoff, R. M., H. A. Wiebe, L. Guise-Bagley, Lidar, nephelometer, and in situ aerosol experiments in southern Ontario, *J. Geophys. Res., 101*(D14), 19199-19209, 1996). We did not find published studies about recent Canadian forest fire (July 2002), analyzed in this paper with which to compare the results. High values of the aerosol extinction coefficient are obtained on vertical profiles during the haze due to Canadian forest fire (reaching sometimes values from 0.4 to 0.7 km^{-1}).

SEAS: UPDATE Three hundred additional samples, representing all valid samples collected at Ponca St. between 19th and 26th of November 2002, have been analyzed since the last reporting period. In order to have a continuous time-series data set, SEAS samples have been split and the second halves were frozen for biological assays during the periods where only one SEAS was sampling. Atmospheric elemental concentration data obtained from SEAS have been entered into the BSSDB along with the appropriate analytical flags. Level II validation is pending. Analysis and comparison of 24-hr filter-based PM1.2 vs. SEAS data are to be completed during the next project period. Several hundred additional samples from the July 2002 intensive have been selected for Metals and Cytokine analyses and are being processed. This will take several months. Choosing which samples to analyze depends on which other data we have and requires time-consuming checks of records for all instruments.

PROGRESS ON BIOASSAY OF SEAS SAMPLES
Cytokine and chemokine responses to NIST standard PM in vitro exposures. Previous results have established dose response curves ranging from 62.5 – 1,000 ug/ml for release of IL-6 and TNF" from RAW264.7 and release of IL-8 and MCP-1 from A549 cells in culture by NIST PM$_{2.5}$ and NIST 1648 samples. During this project period, dose response curves for cytokine and chemokine responses were conducted at lower PM concentrations from 1 to 62.5 ug/ml. Over this lower range, there was no significantly increased release of IL-6 in RAW264.7 cells, while TNF" release increased in a dose responsive manner starting with a significant increase at 10 ug/ml. The TNF" response to NIST PM$_{2.5}$ samples was greater than the response observed at the same concentration of PM 1648 samples.

Results obtained from A549 cells exposed over the same lower concentration range (1 – 68.5 ug/ml) indicated that exposure to the NIST PM$_{2.5}$ samples stimulated the release of IL-8 at 15 ug/ml and higher; however no IL-8 response was observed in cells exposed to the PM 1648 samples over this concentration range.   Release of MCP-1 was stimulated by both types of particles, however, at

concentrations of 15 ug/ml and above, with a greater stimulation observed in cells exposed to the NIST $PM_{2.5}$. This difference between the two types of PM samples in the A549 cells was consistent with their effect on cell metabolism as measure by the Alamar blue assay. No decreased cell metabolism was observed over the 1 to 68.5 ug/ml range in cells exposed to PM1648, while metabolism was decreased in cells exposed to NIST $PM_{2.5}$ above at concentrations above 15 ug/ml. The greater effects observed in response to the NIST $PM_{2.5}$ particles may be due to a number of differences between the two NIST particle samples, including differences in chemical composition and/or particle size.

Baltimore ambient $PM_{2.5}$ modulates cytokine and chemokine responses. Earlier work has shown that $PM_{2.5}$ collected by the SEAS instrument over short (30 or 60 minute) time intervals at the Baltimore Supersite Ponca Street site differed in their bioactivity as measured by their ability to stimulate cytokine and chemokine release in our RAW264.7 and A549 cell culture systems. These results suggest that the health effects of inhaled air particles will vary within a 24 hr time period, reflecting variations in chemical composition of the particles derived from different local sources which can change thoughtout a day. During this project period, we completed the analysis of a series of SEAS samples collected during November and compared results from our July intensive
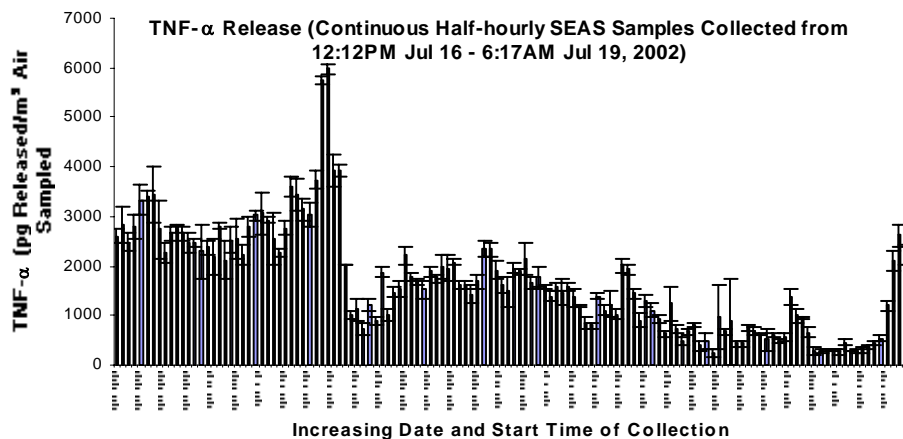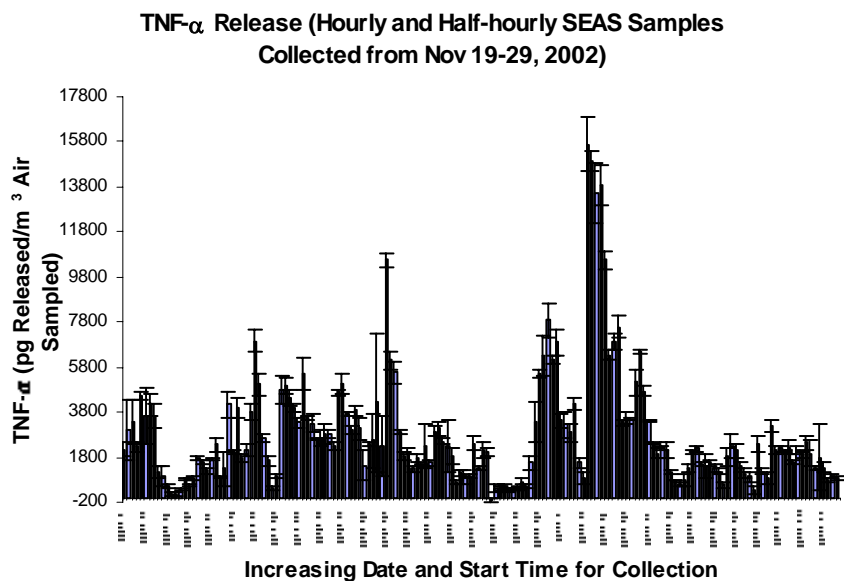

Figure 2

Figure 3

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sampling period. This comparison provided us with information on seasonal differences in Baltimore $PM_{2.5}$ bioactivity. Results showed that $PM_{2.5}$ samples collected over two 4-day periods in November were, in general, more reactive than those collected in July, particularly during episodes on Nov 24th, 26th and 29th when TNF" release from RAW264.7 cells peaked at concentrations about 2.5 fold higher than the highest concentrations measured in studies with the July samples (Figures 2 and 3).

MCP-1 release from A549 cells also differed for $PM_{2.5}$ collected in July versus November. There was little to no significant increase or decrease in MCP-1 release by July samples compared to November samples which significantly inhibited MCP-1 from 500 to 3,000 pg/m^3. (Figure 4 and 5).

The basis for the seasonal differences in the observed responses is being explored. Analysis of samples for endotoxin concentration has shown a greater variability in November samples compared to concentrations in July. In addition, preliminary statistical analysis was conducted examining correlations between the metal ion content of the $PM_{2.5}$ samples and effects on MCP-1 and TNF" release in cultured cells. A comparison of the concentrations of eleven metals measured by GFAAS revealed that Al, Fe, and Zn were the most abundant metals in both the July (Fe>Al>Zn) and the November (Fe>Zn>Al) samples. Statistical analyses demonstrated significant Pearson correlations (P<0.05) between ambient Fe and Cu concentrations and subsequent
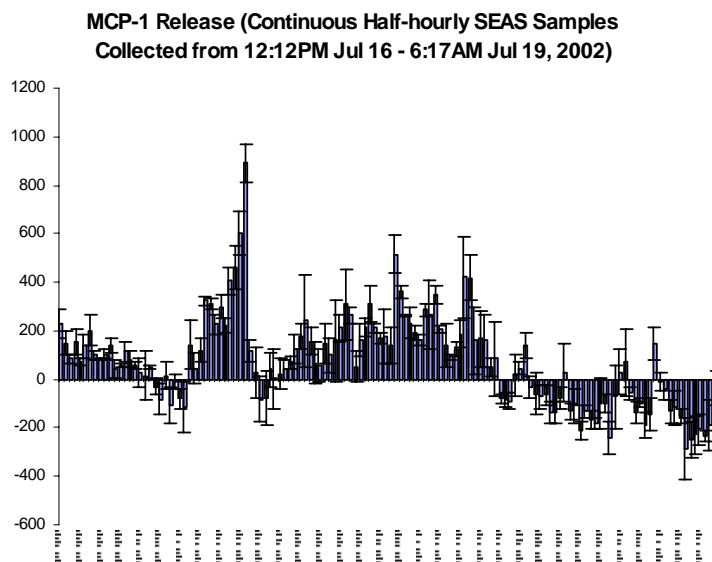

MCP-1 Release (Continuous Half-hourly SEAS Samples Collected from 12:12PM Jul 16 - 6:17AM Jul 19, 2002)

Figure 4

MCP-1 Release (Hourly and Half-hourly SEAS Samples Collected from Nov 19-29, 2002)

MCP-1 (pg Released/m³ Air Sampled)
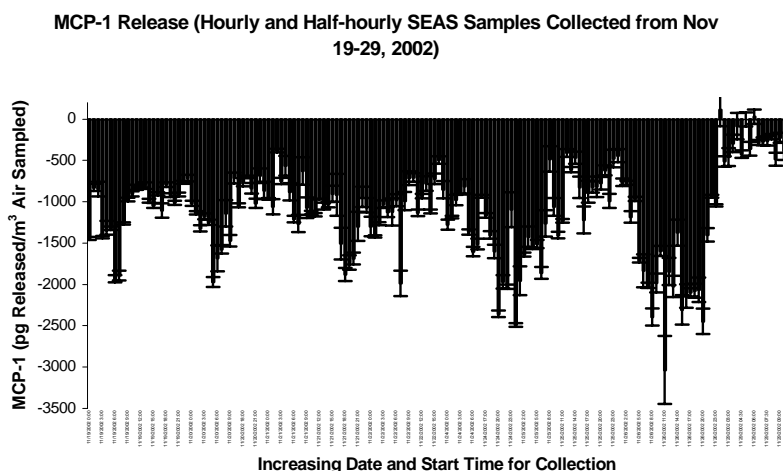
Increasing Date and Start Time for Collection

Figure 5

TNF" and MCP-1 release for both sampling periods. Ambient Al concentrations from both July and November correlated with TNF" release. In contrast, Zn correlated well with TNF" released in response to the November samples (r = 0.507) and MCP-1 released in response to the July samples (r = -0.576).

OTHER DATA:
The following data sets need to be loaded into BSSDB: 10-min MDE GC VOC data, SEAS Cytokine response data, Organic Compound analysis data, Drum impactor synchrotron XRF data, and VOC canister data. In addition, all forward scattering aerosol spectrometer data collected at FMC and Clifton Park have been normalized to logarithmic bin widths and require reloading into BSSDB. Lastly, I RSMSIII file needs to be repaired and loaded.

MULTIVARIATE DATA ANALYSIS
UMCP Pseudo-Deterministic Receptor Model. During this quarter, UMCP developed a new multivariate pseudo-deterministic hybrid receptor model to resolve the contributions of pollutants from individual stationary sources using ambient measurements made at temporal provided by the UMCP SEAS. In the model ambient concentrations are reconciled against the products of their emission rates and atmospheric dispersion factors for individual sources in a receptor equation, wherein values of the latter are estimated from a Gaussian plume model and used to constrain the solutions. In contrast to factor analysis models, the new hybrid model explicitly uses knowledge of wind direction in relation to that of the known sources, as well as other plume dispersion variables, yet preserves the robustness of a least-squares fit to the ambient data.

Our goal was to determine the emission rates of species, i, from stationary sources, j, using highly time-resolved concentration measurements derived from the UMCP SEAS or other highly time-resolved measurements, such as FRM SO_2 monitors. The basis of the model is a mass balance equation such that the ambient contributions of each of the sources to each species are expressed as products of emission rates ($ER_{i,j}$, g/s) and meteorological dispersion factors ($P/Q_{j,t}$, s/m^3) appropriate for each for each sampling period t, i.e.,

$$[E_i]_t = \sum_{j=1}^{n} ER_{i,j} \cdot \chi/Q_{j,t} + [E_{bkgnd_i}]_t \qquad (1)$$

As such, ER_{ij}s represent averages for the period during which the 18 samples (time intervals) used in model were collected. To solve the model, $P/Q_{j,j}$'s are calculated for each sampling interval using a simple Gaussian plume model

$$(\chi/Q)^{Met} = \frac{1}{\pi \sigma_y \sigma_z u} \exp[-\frac{1}{2}\frac{y^2}{\sigma_y^2}] \cdot \exp[-\frac{1}{2}\frac{H^2}{\sigma_z^2}] \qquad (2)$$

where the mean transport velocity (u), standard deviations of plume width and height (s_y and s_z), and

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plume elevation (H) are calculated from micrometeorological and source data using standard formulae.[4] Results of Equation 2 are used to constrain the solution to Equation 1 as follows:

$$(\mathbf{X}/Q)_{j,t \text{ Eq 1}} = C_j \ (\mathbf{X}/Q)_{j,t}\text{Met} \quad \text{where} \qquad 0.1 < C_j < 2$$

As applied to the Tampa BRACE data, the model was solved to obtain a set of 72 emission rates (i.e., 12 species for each of the 6 sources) and for a set of 108 $\mathbf{X}/Q$s (18 for each of 6 sources). Emission rates predicted for SO_2 and 11 aerosol-particle-borne elements are listed in Table 1.

The model was tested on FRM SO_2 and metals measurements (Al, As, Cr, Cu, Fe, Mn, Ni, Pb, Se, and Zn) made with the UMCP SEAS at the Bay Regional Atmospheric Chemistry Experiment site in Tampa, Florida. Data representing the period 12:00 and 20:30 hours on May 13, 2002 were selected for use in the model. During this period, the wind angle traversed the SW sector (200-260°), in which four large utility scale power plants, a battery recycling plant, and a fertilizer plant are located. Model outputs were time-dependent plume dispersion factors (X/Q) for each of the 6 sources, average emission rates for SO_2 and the 11 aerosol species for each source during the analysis period, and ambient concentrations calculated as their products.

As indicated in Table 3, agreement between predicted and observed ambient SO_2 concentrations was excellent: the correlation coefficient (R^2) was 0.97, and their ratio was 1.00 ± 0.18. Moreover, the predicted SO_2 emission rates for each of the 6 sources lie within 10 % of the average continuous emission monitor values except those for the Manatee plant (for which it was within 30%). For elemental markers of coal- (As and Se) and oil-fired (Ni) power plants emissions, the average ratio of predicted and observed concentrations was 1.02 ± 0.18 for As, 0.96 ± 0.17 for Se, and 0.99 ± 0.41 for Ni,

Table 3. Predicted emission rates of SO_2 and metal species (unit : g/s) for Tampa area test case.

Species	Gannon	Bartow	Big Bend	Manatee	Cargill	Gulf coast
SO_2 (obs.)[1]	2600	1100	303	1280	40[2]	25[2]
SO_2 (pre.)	2490	1150	305	930	45	32
Al	1.109	0.151	1.229	6.946	0.058	0.042
As	0.031	0.032	0.019	0.006	0.001	0.001
Cr	0.029	0.027	0.026	0.167	0.002	0.001
Cu	0.005	0.004	0.036	0.085	0.003	0.001
Fe	1.146	0.401	1.246	5.853	0.077	0.041
Mn	0.003	0.002	0.022	0.180	0.001	0.001
Ni	0.002	0.002	0.032	0.604	0.002	0.001

Pb	0.007	0.006	0.067	0.138	0.004	0.003
Se	0.032	0.032	0.002	0.043	0.001	0.001
Zn	0.018	0.018	0.113	0.760	0.005	0.003

[1]Average continuous emission monitor data from the stacks (12:00~21:00 hr May 13)
[2]Annual average SO2 emission data (not CEM data)

respectively, indicating that the 6 sources located in the wind sector between 200~260° well accounted for concentrations measured at the sampling site. The excellent results for SO_2 suggest that the new sampling and modeling technology promises to be an important tool for providing emission rates for other species, i.e., without expensive in-stack sampling or continuous emission monitoring, needed for EPA's toxic emission inventory. Accurate dispersion parameters provided by the model are useful in dispersion model development. In the Tampa study, estimates of emission rates of SO_2 and primary particle-borne elements from 6 individual stationary sources affecting Tampa Bay air quality were made with only 18 observations, i.e., far fewer than needed for Factor Analysis methods.

Future Plans. We intend to apply the model to our somewhat more complex Baltimore Supersite data during the next quarter.

Clarkson Analysis of Data from Different Sampling Time Intervals. One of the more interesting aspects of the Supersite exercise is the production of data from samples taken over varying duration time intervals. Traditional multivariate techniques (PCA, PMF2) cannot utilize the full information content of data sets measured with multiple sample time schedules. It would be necessary to somehow transform the data to a single time schedule. Either the high-resolution data need to be averaged over the averaging intervals of the longest time-interval data, typically 24 hours, or the low-resolution data would have to be interpolated to the short time periods of the fastest measurements. Averaging would lose all of the valuable high time-resolution information. Alternatively, interpolation must base on uncertain assumptions of the nature of temporal variation of the source emissions. Interpolation would typically ignore diurnal patterns and attribute similar amounts of concentration to all 24 hours of the sampling period. Thus, it would be impossible to correctly deduce the proper connections between the 24-hour interpolated aerosol data and high-resolution (e.g., hourly) concentration data displaying the true short term patterns.

Model Description

The basic idea is to utilize the measured concentration data in its original time schedule. For each concentration value, there are contributions from several sources and source contributions have to be averaged so that the concentration value and the source contribution are in the same sampling period. The main equation of the model is as below:

$$x_{sj} = 1/(t_{s2} - t_{s1} + 1) \sum_{p=1}^{P} \left(f_{jp} \sum_{i=t_{s1}}^{t_{s2}} g_{ip} \, \eta_{jm} \right) + e_{sj} \tag{1}$$

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where s is the sample number, j stands for the species, t_{s2} is the end time unit and t_{s1} is the start time unit. The shortest sampling interval, 10 min for this data set, is chosen as the time unit. In Equation 1, x_{sj} is the concentration of jth species in sth sample, f_{jp} is the mass fraction of species j in particles from source p, g_{ip} is the pth source mass contribution during the time units for the sth sample and e_{sj} is the residual. The source contributions are averaged over the sampling time of x_{sj}. If all species of all samples are measured within same durations, $t_{s2}=t_{s1}$, then Equation 1 becomes the conventional two way receptor model.

Replicated species were measured by more than one method with different time resolution. In Equation 1, different values of the subscript m correspond to different measurement methods (for ADI data $m=1$, for SEAS data $m=2$ and for steam IC $m=3$). For each sample s, the m value corresponds to the method used for measuring the sample, $m=m(s)$. For a replicated species j, adjustment factors, $\boldsymbol{O}_{jm}$ in Equation 1, are used with the assumption that the concentration values measured by different methods are proportional. An adjustment factor close to 1 suggests a good agreement between the different measurements. Usually, the methods with longest periods provide better accuracy or are defined as reference methods. Thus, their adjustment factors are set to unity by default. For non-replicated species, no adjustment factors are needed, so that their $\boldsymbol{O}_{jm}$ are set to unity by default.

If a source contains no species measured with high temporal resolution, then there is no way to obtain a reliable high time resolution contribution series. To solve this problem, a regularization equation is used to smooth the time series of source contributions, as indicated by Equation 2, where g_{ip} is the source contribution from the pth source during the ith time unit.

$$g_{i+1,p} - g_{i,p} = 0 + \varepsilon_i \tag{2}$$

The total residual sum of squares is composed of residuals from both Equations 1 and 2. When a source includes few high time resolution species, there is limited influence from Equation 1 and Equation 2 will eliminate the unreliable high time resolution details of the contribution series in order to minimize the residuals. When a source contains some high resolution species, reducing the residual in Equation 2 leads to an increase in the residuals of Equation 1 and the high temporal variation tend to be conserved. The balance between the two residuals can be controlled by multiplying the residual in Equation 2 by a small coefficient, such as ~0.1. This balancing was implemented by weighting the residuals with their uncertainties.

The model was solved using the Multilinear Engine (Paatero, 1999). A script file was written to specify the model equations. The final weighted sum square of residuals (Q) is optimized by a conjugate gradient method (Paatero, 1999). This approach has been tested with a small set of data from Pittsburgh. However, the results were limited by the relatively small data set that has been available. Thus, the larger data sets that will be available in this study should permit better tests of the model to provide enhanced source identification and apportionment.

We are currently putting together data sets from the various measurement campaigns. The analysis will be enhanced by the inclusion of the elemental data from the SEAS sampler so the initial exploration will be of the period of March to November 2002. It will take some time to organize the data, develop the error models, and test the model, but we anticipate that over the next months we should have substantial results from this approach.

SUPERSITES RELATIONAL DATABASE

The available supersites data was loaded, but had to be completely reloaded owing to database structure changes. During the reload, many files were identified as having either format or sanity (i.e., range values invalid). Some of these files were corrected and reloaded, but we are still waiting on NARSTO for newer versions of some files. After making a beta version of the generalized query available, additional problems were found with the data, specifically data were not categorized correctly owing to conflicting or vague column definitions. We are currently working on an alternative to using NARSTO files for supersites data that will correct these problems.

For non-supersites data, we have received and loaded the NOAA Profiler data. This data also had problems during loaded which necessitated retransmission of the complete set of data from the source. The data has since been loaded and is accessible via the generalized query. AQS data are being analyzed and will be loaded into the database shortly.

Data Statistics.
Supersites data received: 136 Files, 4,405,074,416 bytes (4.4 GB).
Non Supersites: 3.52 GB (3,782,438,912 bytes) NOAA Profiler
                                   2.08 GB (2,234,082,268 bytes) AQS
                                   155 MB (162,814,953 bytes) Improve
Smaller amounts of data from
   ASACA (Assessment of Spatial Aerosol Composition in Atlanta)
   HSPH (Boston Center)
   LADCO Aircraft data
   March-Atlantic data
   NETL (Suburban Pittsburgh, PA), In-House Monitoring Site
   Potsdam_&_Stockton
   RAMMPP(Regional Atmospheric Measurement Modeling and Prediction Program)
   SCAMP(Steubenville OH, Steubenville Comprehensive Air Monitoring Project)
   SEARCH
   TCEQ
   TVA (Tennessee_Valley_Authority)_PM2.5_Partnership
   UORVP(Upper_Ohio_River_Valley_Project)

Future Plans. We will continue to acquire and load Supersites and remaining non-supersites data.

PONCA ST. SEMICONTINUOUS SULFATE DATA:
The semi-continuous Harvard Sulfate monitor was used for all Sulfate measurements made at the Ponca St. site.

Principle of operation. The basic principle of operation is that sulfate is reduced to SO_2 in the presence of stainless steel at elevated temperature, and the eluent is detected with a commercial SO_2 analyzer. A schematic diagram of the prototype instrument employed in this study is shown in **Figure 1**. Air is drawn into the instrument by a pump located in the analyzer at approximately 0.55

L min^{-1}, first passing through a 2.5 **:** m cut. The air stream is then denuded of ambient SO_2 (an interference) *via* a sodium carbonate coated annular glass denuder, and of NO_X (the sum of nitrogen dioxide (NO_2) and nitrous oxide (NO)) by a carbon denuder (optional: see Section 2.3.2 below). The sample is then passed through the converter (a 1.8 m 1/8" o.d. resistively heated stainless steel tube), before detection of the eluent SO_2 by a TEI 43CTL trace level SO_2 analyzer (Thermo Electron Instruments, Franklin, MA, USA). To back out the false-positive analyzer response to gas phase compounds that may also form SO_2 in the heated zone, the airstream is alternated on a 20 minute cycle between 14 minutes of unfiltered air, and 6 minutes of HEPA filtered air (*via* a separate 0.8 L min^{-1} intake located next to the main intake, with the excess flow escaping through a vent). A solenoid valve is used to switch between filtered (*i.e.* zero) and unfiltered (*i.e.* sample) air streams. The sulfate concentration is therefore proportional to the response of the analyzer to unfiltered air minus the response of the analyzer to filtered air. The output voltage of the analyzer and a voltage corresponding to the solenoid position were logged to a computer as 15 second averages using a model 6034E PCI PC ADC card (National Instruments Co.),. The custom written logging software (OSL, Whitehouse Station, NJ, USA) automatically converted Volts to SO_2 / ppbV by application of a 50 multiplier (as dictated by the user-defined settings on the analyzer), and started a new file at midnight each day.

Limitations of the Method. Laboratory measurements at Harvard School of Public Health (HSPH) showed that 100 % conversion of ammonium sulfate aerosols occurred at temperatures exceeding 1000 ℃. 1 mole of $(NH4)_2SO_4$ aerosol is, therefore, converted to one mole of SO_2. For the prototype instrument employed in this study, conversion was achieved using a standard converter (Thermo Electron Instruments, Franklin, MA, USA), which was initially designed to convert NO_2 to NO. Efficiency of conversion is expected to drop over a period of time, as the converter becomes exhausted (Mark Davey, HSPH, personal communication).

As supplied, the TEI 43CTL trace level SO_2 analyzer is optimized to be highly sensitive to SO_2, but has a rejection ratio to NO of 40:1. During the 11 month operation of the sulfate instrument, maximum non-averaged ambient NO_X (The sum of NO and NO_2) concentrations occasionally exceeded 1 part per million by volume (ppmV). As discussed above, NO_2 will be converted to NO in the converter; therefore, at such high ambient NO_X concentrations the interference of NO on the analyzer will be significant. As such, the analyzer was modified by replacing the bandpass filter to have an NO rejection ratio of 400:1, but which reduced SO_2 sensitivity approximately 3-fold. To increase the sulfate detection limit, on 15 May 2002, the instrument was modified by refitting the original bandpass filter in the analyzer and employing a honeycomb carbon denuder (MAST, UK) to remove NO_X from the sample stream. When utilized, the carbon denuder was positioned after the sodium carbonate denuder, as SO_2 had been shown to poison the carbon denuder (Eric Edgerton, personal communication).

As oxygen is present, we assume that ammonia (NH_3) and other gas phase nitrogen containing compounds are oxidized to NO or NO_2 and that any NO_2 formed diffuses to the wall of the converter, where it is converted to NO. As with gas phase sulfur containing compounds, this false-positive response was backed out by alternating between filtered and unfiltered air (Section 2.3.1). Ammonia is also produced by the thermal decomposition of both NH_4SO_4 and ammonium nitrate (NH_4NO_3) aerosols. As 1 mole of ammonium sulfate aerosol will form one mole of NO, this will

increase the apparent conversion efficiency of the method. 1 mole of NH_4NO_3 aerosol will actually be converted to 2 molecules of NO in the converter, and therefore cause an interference to sulfate measurements. Nitric acid will be removed by the sodium carbonate denuder. Problems due to NO interference were more pronounced when the analyzer has only a 40:1 rejection ratio to NO (*i.e.* after 15 May 2002).

Data Reduction and Calculation of Measured Sulfate Concentrations. The daily raw 15 second data files (including the date/time, analyzer output (SO_2 / ppbV), and solenoid position), were imported in to a SQL database (Microsoft, Inc.). A database application (OSL, Whitehouse Station, NJ) was written to calculate sulfate concentrations from the raw data-stream. Large lots of data were processed in a single program run to minimize analysis losses for samples at the beginning and end of the record set.

Calculation of Net SO_2 Concentration (SO_{2net}). The 15 second data-stream was reduced to discreet 20 minute data by calculating the net response of the analyzer to SO_2 (SO_{2net}) upon switching between filtered and un-filtered air. As the solenoid position changes, the instrument displays a finite response time due largely to its internal flow path volume, which imparts a delay between the time the switching valve is activated and the time SO_2 is detected. Further, the time required to achieve background signal conditions is variable as it depends on the ambient sulfate concentration. To deal with these conditions, we constructed the program to first define the start of the sample and background averaging intervals using predetermined offset values and then find the midpoint record for each interval. A halfwidth parameter is then used to control the number of records to be included on either side of the midpoint interval. Use of these parameters allows one to achieve analysis without precise knowledge of the true lag time for each set of sampling and background records.

The solenoid voltage switches between a low (not necessarily zero) voltage and a high voltage (about 1.7 V) when switching from sampling to background mode and visa versa. As both high and low voltages drifted, suitable threshold voltages were applied before analyzing the data.

Accounting for the response time and solenoid voltage thresholds, the program automatically calculates the average SO_2 (ppbV) for each sampling and background interval. A single background value is then computed as the average of the background intervals immediately before and after the sampling interval, and this is subtracted from the average for the sampling period. Standard deviations are calculated for each interval and propagated to produce a measure of uncertainty in the net result.

Data Flagging. Once the raw data-stream was reduced to discrete 20 minute data, they were manually flagged using database applications on the basis of the information from the operator's log. Specifically, the data was flagged void or questionable due to: auditing, calibrating, power outage, excessive NO_X interference, instrument switched off before 20 min sample completed, the analyzer had an electrical fault, a leak was noticed as part of the audit, or either the zero-air flow or oven temperature were out .

Calculation of Measured Sulfate Concentrations (Sulfate$_{measured}$). The analytical equation used to calculate the measured sulfate concentration is shown below.

$$\text{Sulfate}_{measured} = AF_i ((1170.6 * SO_{2\,net} * (P_{amb}/T_{amb})) - (3.10 * \gt_{nitrate} * [\text{Nitrate}] / R_{NO}))$$

Where:

Sulfate$_{measured}$ is the measured sulfate concentration (in $: g\,m^{-3}$) before correcting to filter samples.

AF$_i$ is a dimensionless audit factor to account for analyzer drift.

1170.6 is a constant (with the units $: g\,K\,m^{-3}\,atm^{-1}\,ppbV^{-1}$), and is calculated as: Molecular weight of sulfate (96 g mole^{-1}) divided by R (0.082058 L atm mole^{-1} K^{-1}) and includes conversions for $:$ g to g, L to m^3 and ppbV to parts by volume.

P$_{amb}$ is the ambient pressure in atmospheres.

T$_{amb}$ is the ambient outdoor temperature in K.

$\gt_{nitrate}$ is the efficiency of ammonium nitrate to NO conversion relative to the conversion efficiency of sulfate to SO$_2$ (dimensionless)

3.10 is a dimensionless constant, and is calculated as the product of the 'moles of NO produced per mole of NH$_4$NO$_3$ (2)' and the 'molecular weight of Sulfate (96 g mole^{-1})' divided by the 'molecular weight of Nitrate (62 g mole^{-1})'.

[Nitrate] is the measured ammonium nitrate concentration in $:$ g m^{-3}.

R$_{NO}$ is the dimensionless rejection ratio of the analyzer to NO (*i.e.* either 400 or 40).

Ambient temperature and pressure were obtained from a meteorological station sited at the Supersite. In cases where these data were missing, information from other instruments was inserted. If no other data were available, a pressure of 1 atmosphere and an interpolated value of the temperature were used.

Correction for drift in analyzer span (AF$_i$). Audit factors, AF$_i$ were calculated as the ratio of the calibration gas (typically 470 ppbV) to the SO$_2$ (ppbV) indicated on the analyzer at the time of the calibration or audit. Values of AF$_i$ were calculated for those specific date and times when the analyzer span was audited or calibrated. Values of AF$_i$ were then linearly interpolated to the date and time of each individual sulfate data record using an Excel Visual Basic macro (Microsoft Inc.). The analyzer was observed to drift by up to 4.3 % over extended periods of time.

Correction for Nitrate interference. Corrections due to the false positive response of nitrate aerosols were made with ambient NH$_4$NO$_3$ concentrations measured using an R&P8400N ambient particulate nitrate monitor (Rupprecht and Patashnick, Albany, New York, USA) after they were corrected to the 24-hr integrated Speciation Nitrate measurements. As NH$_4$NO$_3$ is far less stable at 800 ℃ than is NH$_4$SO$_4$, it is likely that the conversion efficiency of NH$_4$NO$_3$ is higher than that of NH$_4$SO$_4$, and so we assumed that the efficiency of conversion efficiency for NH$_4$NO$_3$ ($\gt_{nitrate}$) is 1. Correction for NO interference from Nitrate-containing aerosol particles was made using a database application (OSL, Whitehouse Station, NJ), employed subsequent to the program that calculated the sulfate concentration.

Correction for ambient NO$_X$. Prior to the installation of the carbon denuder on the 16 May 2002, any ambient NO$_X$ will be converted to NO, and detected by the analyzer. For this period, the analyzer had been modified to reject NO at a ratio of 400:1. At this rejection ratio, provided NO$_X$ concentrations are relatively constant over the 20 minute sampling period, there should be little increase in the sulfate detection limit. However, as explained in Section 2.3.2, maximum NO concentrations occasionally exceeded 1 ppmV, and these events typically lasted on the order of seconds. NO$_X$ was measured at the Supersite as 10 minute averages, which is longer than the 6 minute blank cycle employed in the semi-continuous sulfate instrument. As such, it was not possible to subtract NO$_X$ interferences from the raw semi-continuous sulfate data-stream; however, periods of significant contamination were flagged as void.

Efficiency Corrections. As there was no provision for direct calibration with a known concentration of sulfate aerosol or for injection of known amounts of mass, this instrument required calibration against 24-hr speciation sulfate concentrations. Comparisons between 24-hr integrated MetOne and averages of the corresponding Harvard sulfate data are shown in Figure 1.

Note that prior to May 15, 2002, when a carbon MAST denuder was installed, sulfate signals were barely detectable above the background signal for most of the data, hence, are largely unusable. This was in large part due to interference by Nitrogen oxides, which was eliminated by the MAST denuder. Prior to this date, the apparent conversion efficiency declined from a high of about 82% to a low of about 3%. After the denuder was installed, the apparent efficiency increased to about 50% from about June 1st until the middle of July, but was highly variable. Afterwards, the apparent efficiency declined to an average of about 35%, but was again highly variable. The stainless-steel converter tubing was replaced on 31 October 2002. Afterwards, the conversion efficiency (average of about 38%) was less variable for approximately 3 weeks, but was lower than measured in June and July.

The conversion efficiency of the unit is clearly temperature dependent. As mentioned above, the original prototype system was operated at 1000ºC, at which the conversion efficiency for ammonium sulfate was reported to be 100%. However, owing to the physical limitations, we operated the converter (Thermo Electron Inc.) at 800 ºC, at which an ammonium nitrate conversion efficiency of 75% was expected. Tests performed in the development of the original prototype showed that the conversion efficiency for sulfate in the form of sulfuric acid was about 25% less than that for ammonium sulfate. Also, metal sulfates were found to be undetectable (David Harrison, private communication). As shown in Figure 6, higher conversion efficiencies were observed in warm months (May through August) than in cold months (Oct ~ Nov). Ammonia emissions are greater in summer than in colder months and are highly variable. Lower ammonia emissions would favor ammonium hydrogen sulfate formation, which can be viewed as a mixture of ammonium sulfate and sulfuric acid. Its possible, therefore, that the highly variable conversion efficiency is the result of variations in aerosol acidity and alkaline dust content.

As indicated in Figure 6, the apparent efficiency varied somewhat less within each month than it did from month-to-month, especially after May 15th. Therefore, we chose to correct the Harvard Monitor data using monthly efficiency correction factors. Analysis of the data collected after May

15th, showed that for all of months the reference speciation sulfate concentrations were highly correlated with the Harvard Monitor values (see Table 1), i.e., $R^2 > 0.89$ for all months except September. Ideally, the conversion efficiencies would simply be the inverse of the slopes listed in Table 4. However the offsets are fairly large, i.e., in the range of 1 to 2 **:** g/m^3 so that the full regression equation is required to correct the data. Prior to May 16th, variability was less.

Table 4. Regression relationship between 24-hr MetOne and Harvard sulfate data in 2002

Month	Regression analysis	R^2	Remarks
May	Y = (1.876±0.298) X + (2.376±0.952)	0.929	
June	Y = (1.596±0.069) X + (0.732±0.313)	0.993	
July	Y = (1.571±0.099) X + (1.395±0.554)	0.901	
August	Y = (1.950±0.072) X + (0.943±0.291)	0.976	
September	Y = (1.217±0.838) X + (1.776±2.256)	0.680	
October	Y = (3.334±0.175) X + (0.995±0.351)	0.992	
November	Y = (2.213±0.152) X + (0.558±0.207)	0.886	

Y (μg/m^3): 24-hr MetOne sulfate; X ((μg/m^3): 24-hr Harvard sulfate

Note that for the September data, regression analysis was not statistically significant, so the regression result was not applied to the sulfate data. Rather an average efficiency factor was used for correcting the September data.

Future work. The final sulfate concentrations, i.e., those determined after all corrections were completed, will be checked for "reasonableness" by mass balance and against PM2.5 mass
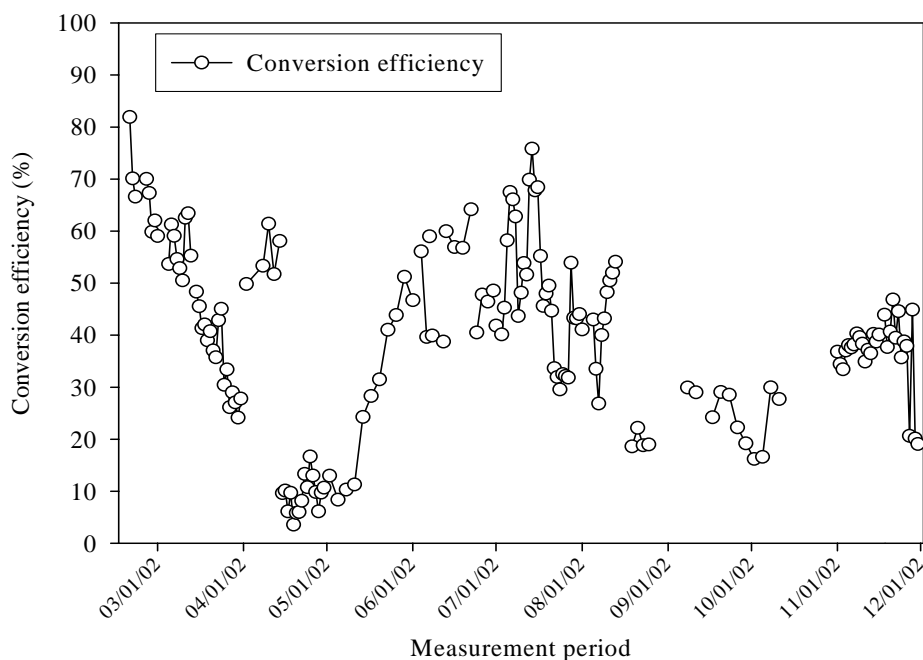

Figure 6. Conversion efficiency of Harvard sulfate monitor in Baltimore

concentrations in the next quarter. Once this process is complete, the data can be submitted to the NARSTO archive.

FILTER/PUF ANALYSES FOR 3-HR RESOLUTION OF ORGANIC COMPOUNDS.
Summer Intensive. All summer samples (139 filter & PUF pairs), including 20 field and transportation blanks (filter & PUF pair) have been extracted, methylated to convert organic acids to their methyl ester analog. The data quantification is completed to about 95%. The data validation process in expected to start at the end of February. Figure 7 shows the ambient concentrations of "vehicular" n-alkanes (C19 - C25) and for alkylcyclohexanes that are as well associated with vehicular emissions. Overall, the concentration profiles for both compound classes follow each other nicely. **(These data need to be validated to become final!)**
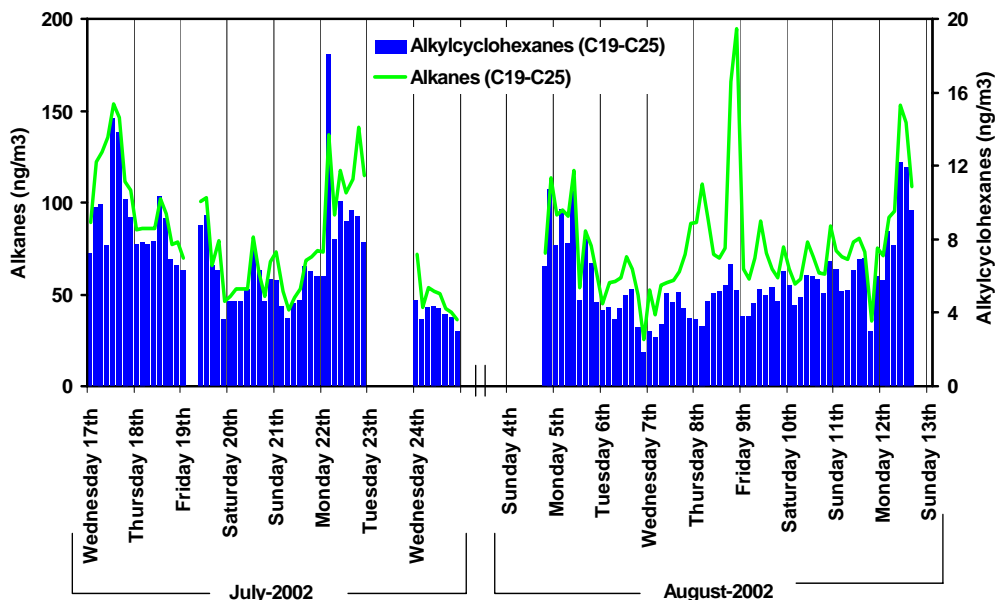
Figure 7

Figure 8 shows ambient concentrations for hopanes versus "vehicular" n-alkanes (C19 - C25). Also here, the hopanes (fossil markers) and the "vehicular" n-alkanes concentration profiles show a similar distribution over time, indicating that most of the time the hopanes are related to vehicular exhaust emissions. The one odd thing about the hopanes is that every Monday morning, between 3 and 6 am, the concentration levels shoot up and do not correlate with the "vehicular" n-alkanes or alkylcyclohexanes. One possible explanation is that refineries blow their "waste" via flares into the atmosphere. The night from Sunday to Monday is the best night to do so. This is the night where most people stay home and therefore will not be aware of a smelly atmosphere. Again, at this point in time, this is pure speculation. (These data need to be validated to become final!)
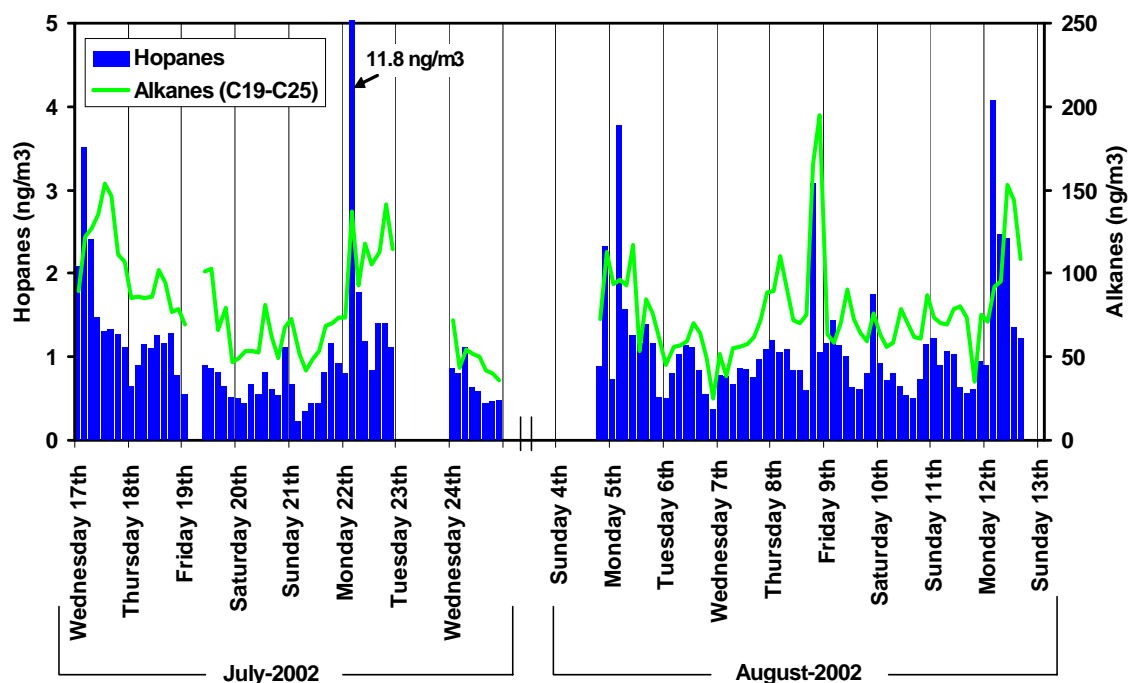
20

Figure 8

Figure 9 shows the three-hourly PAHs (from phenanthrene to coronene) concentrations over the summer intensive. **(These data need to be validated to become final!)**
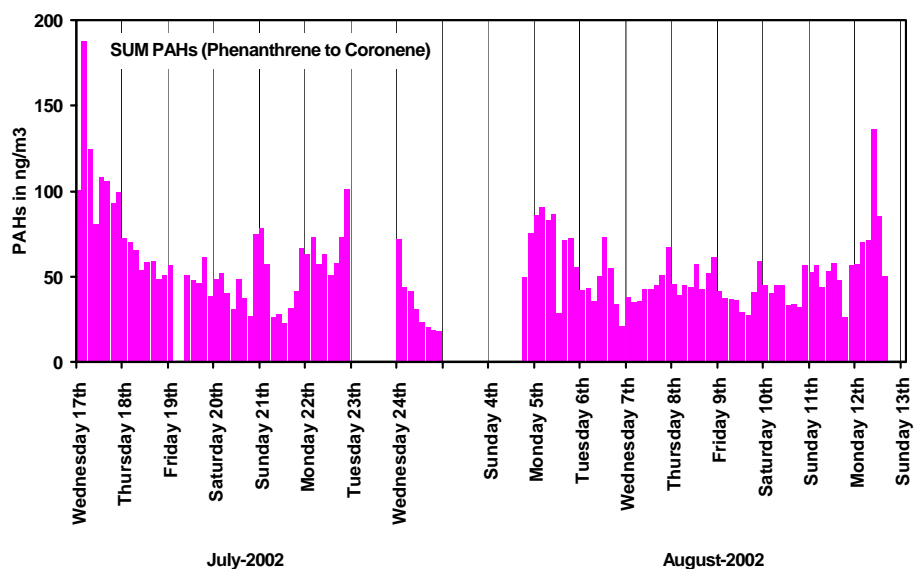

Figure 9

Winter Intensive. For the winter intensive, a total of 136 filter and PUF pairs have been extracted, including 17 field and transport blanks. All sample extract have been methylated. So far, we run 35 extracts of filter and PUF pairs on the GC/MS. For those 35 sample pair chromatogram interpretation and data quantification is already in progress.

Manuscripts planned. We are getting a lot of ambient data that cannot be summarized in just one paper. The plan is to produce approximately 4 papers dealing with summer, winter, seasonal, and correlations with other environmental parameters, etc. Another batch of papers should then be written, including some of your data and data from others, that can highlight source contributions to the sampling site and atmospheric conversion of organic matter. Lastly, a manuscript entitled, Sequential Organic Sampler for 3-hr Time Resolved Organic Species Measurements, Yu Chen Chang, W. Rogge, J. M. Ondov, is being prepared.

PUBLICATIONS (Cumulative)
Mitkus RJ, Powell JL, Zeisler R, Squibb KS, Differences in the biological activity of NIST
Interim   Reference Material (PM2.5) and NIST Standard Reference Material 1648 (urban
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                  preparation.

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          activity of ambient PM2.5 collected by a high frequency aerosol sampler. The
          Toxicologist 66: 359, 2002.
Mitkus, R., Powell, J., Akkerman, M. and Squibb, K. Differential in vitro immunological
          responses to zinc (Zn), an active component of urban particulate matter (PM). Tox. Sci.
          72 (S-1), 299, 2003.
Markus Pahlow, Jan Kleissl, Marc B. Parlange, John M. Ondov and David Harrison. Atmospheric
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          Accepted by Boundary Layer Meteorology.

D.A. Lake, M.P. Tolocka, M.V. Johnston, A.S. Wexler, "Mass Spectrometry of Individual
          Particles Between 50 and 750 nm in Diameter at the Baltimore Supersite," Environmental
          Science and Technology (2003) 37, 3268-3274

M.P. Tolocka, D.A. Lake, M.V. Johnston, A.S. Wexler, "Number Concentrations of Fine and
          Ultrafine Particles Containing Metals" Atmospheric Environment (2003) in press.

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          Baltimore Observed by Real-Time Single Particle Mass Spectrometry", Atmospheric
          Environment (2003) in press.

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          in Baltimore", Atmospheric Environment (2003) submitted.

M. P. Tolocka et. al., Particle classes in Baltimore, to be submitted by the end of January to the special JGR issue.

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Park, S. S., Ondov, J. M., Carbon species and CO emission factors derived from the Canadian forest fires. To be submitted to the special JGR issue in January 2004.

Park, S. S., Harrison, D., Ondov, J. M., Seasonal and short-term variations in Nitrate concentrations. Seasonal and short-term variations in Nitrate concentrations.

Murray Johnston Group: Size resolved ultrafine particle composition analysis part 3: Baltimore, To   be submitted to the special JGR issue in January 2004.

Mitkus RJ, Powell JL, Ondov, JM., Pancras, JP. and Squibb KS. Baltimore $PM_{2.5}$ daily and seasonal variations in *in vitro* stimulated chemokine and cytokine release: Correlation with metal content. In preparation

PRESENTATIONS/MEETINGS
INTERNATIONAL SOCIETY OF EXPOSURE
Sapkota, A.; Symons, J.M.; Kleissl, J.; Wang, L.; Parlange, M.; Ondov, J.; Buckley, T.J.; The Impact of Canadian Forest Fires on Air Pollution in Baltimore City: A Case Study of Long-range Pollutant Transport. 13th Annual Conference International Society of Exposure Analysis. Stresa Italy, 2003.

EGS-AGU, 2003
.   Adam, M.; Pahlow, M.; Kovalev, V.; Ondov, J.; Balin, I.; Simeonov, V.; van den Bergh, H.; Parlange, M. Determination of the Vertical Extinction Coefficient Profile in the Atmospheric Boundary Layer and the Free Troposphere" Presented at EGS-AGU, 6-12 April 2003, Nice, France

.   Mariana Adam, Markus Pahlow, Marc Parlange, John Ondov, "Atmospheric Boundary

Layer characterization during the Baltimore PM Supersite - July 2002" AAAR, 31 March - 4 April 2003, Pittsburgh, PAP11-16

Society of Toxicology Meeting, March 2003, 2004

R Mitkus[1], J Powell[1], J Ondov[2], and K Squibb[1]. Seasonal Metal Content Measured in Baltimore PM$_{2.5}$ SEAS Samples Correlates with Cytokine and Chemokine Release Following Exposure to Fine Particulate Matter in an *In Vitro* Assay System. Accepted for presentation at the Society of Toxicology Meetings, March 21-25, 2004.

R Mitkus, J Powell, M Akkerman and K Squibb. Differential Immunological Response of Two Airway Cell Types to Zinc (Zn), an Active Component of Urban Particulate Mattter (PM). To be presented at the Society of Toxicology annual meeting, March 9-13, 2003.

AAAR Meeting, March 2003 .

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Turner, J. R., Allen, G., Bahadori, Chow, J. C, Hansen, D. A., Husar, R. B., Koutrakis, P., McMurry, P. H., Ondov, J. M., Schauer, J. J.,Watson, J. G.,, Weber, R. J. White, W. H., (2003). Overview of the Saint Louis Midwest Supersite. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmospheric Sciences, Exposure, and the Fourth Colloquium onPM and Human Health, March, Pittsburgh.

Park, S. S., Harrison, D., Ondov, J. M., Tolocka, M. P., Lake, D. A., Johnston, M. V. (2003) Transient Elevations in the Concentrations of Sulfate, Nitrate, and EC/OC Measured with Semicontinuous Monitors at the Baltimore Supersite. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmospheric Sciences, Exposure, and the Fourth Colloquium on PM and Human Health, March, Pittsburgh.

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